

Electrochemical modelling using electroneutrality equation as a constraint

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Abstract This paper deals with ionic species migration based on classical mass balance equations in conjunction with a charge balance equation and the electroneutrality condition. Two new methods are proposed to apply the electroneutrality condition, avoiding the elimination of one of the conservation equations of chemical species and permitting to explicitly apply boundary conditions on all species. The first method is based on variational principles and the second on a Lagrange multiplier. It is shown that the new methods are analytically equivalent to the more standard method in which one conservation equation is eliminated without any other consideration. The variational method is more complex to implement than the Lagrange multiplier method. The new methods were applied to a multi-ionic problem together with the charge conservation equation without capacitive effects. Different kinds of boundary conditions were applied: Neumann, Dirichlet and a nonlinear case based on Butler–Volmer kinetics. All methods gave the same results for non-complex problems. In the case of complex problems including chemical equilibrium between each ionic species, it was found that more investigations are necessary even for more conventional methods.

Keywords Electroneutrality · Finite element method · Lagrange multiplier · Electrochemical engineering · Variational method

List of symbols

\vec{x}	Position (m)
t	Time (s)
L	Domain size (m)
V	Volume (m^3)
A	Area (m^2)
Γ	Boundary area (m^2)
$c_i(\vec{x}, t)$	Concentration of species i ($mol\ m^{-3}$)
N	Total number of ionic species
R	Rate of reaction ($mol\ m^{-3}\ s^{-1}$)
s_i	Stoichiometric coefficient for species i
D_i	Diffusion coefficient of species i ($m^2\ s^{-1}$)
\vec{J}_i	Molar flux of species i ($mol\ m^{-2}\ s^{-1}$)
\bar{J}_i	Boundary molar flux of species i ($mol\ m^{-2}\ s^{-1}$)
u_i	Mobility of ionic species i ($J\ m^2\ s^{-1}\ mol^{-1}$)
z_i	Charge number of species i
F	Faraday's constant ($C\ mol^{-1}$)
Φ	Solution potential (V)
Φ_s	Electrode surface potential (V)
U	Equilibrium potential (V)
\bar{R}	Gas constant ($J\ mol^{-1}\ K^{-1}$)
T	Temperature (K)
i_0	Exchange current density ($A\ m^{-2}$)
η_s	Surface overvoltage (V)
α_a	Apparent anodic transfer coefficient
α_c	Apparent cathodic transfer coefficient
\vec{i}	Current density ($A\ m^{-2}$)
\bar{i}	Boundary current density ($A\ m^{-2}$)
W	Total weighted residual
W_c^i	Species i conservation equation weighted residual

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W_Φ	Charge conservation equation weighted residual
λ	Lagrange multiplier
K	Ionic equilibrium constant

1 Introduction

In the research field of electrochemical systems modelling, there is a need to evaluate the species concentration variables and the potential or current density across a well-defined domain and under different boundary conditions with or without chemical equilibrium equations to satisfy. Models of this kind normally have at least one species conservation equation for each species and another equation used to obtain the potential or the current density. More complex models require some additional partial differential equations such as the fluid dynamic equations and an energy conservation equation, for example. Complementary to these conservation equations, other equations are necessary such as constitutive relations to define species flux. To build this kind of model, some other issues have to be addressed. For example, is it that the system remains macroscopically electroneutral and/or are there some capacitive effects to be taken into account? The answer to the last question depends on the spatial scale of the system modelling. For example, already charged porous media will be electroneutral and will not experience capacitive effects for a sufficiently large spatial modelling scale. However, if the porous medium is not already charged, some capacitive terms could be necessary even if the model is built for some sufficiently large spatial scale to remain electroneutral [1]. An opposite example would be the modelling at a sufficiently small spatial scale of a double layer electrode interface where capacitive effects would exist with the domain not locally electroneutral. In this paper, only non-capacitive systems are discussed.

One of the main questions in an electrochemical system is how to obtain the potential or current density distribution. One part of this problem is to define constitutive laws for the current density as a function of the potential. (The case where the model is solved directly for the current density vector components [2] is not discussed). There are three main equations or some combination of them used to answer the last question. These three equations are Gauss's law, the charge conservation equation and the algebraic electroneutrality equation. The use of Gauss's law is more difficult and not recommended [1] because it can induce numerical instabilities due to the large value of the Faraday constant and permittivity ratio. Nonetheless, some systems have been modelled with success using the Gauss's law approach [3–6]. The present paper is not addressing this

kind of model in detail, and it is only partially discussed. The next paragraphs focus on the modelling of electrochemical systems using an algebraic electroneutrality equation with or without the charge conservation equation.

First of all, the different electrochemical systems of interest are further classified into two different kinds of application: with an applied current and no net current. The electrochemical models with no net current have already been addressed thoroughly in the literature related to the fields of geochemistry and chemical oceanography by Boudreau et al. [7, 8]. The only remark on this paper is that this kind of ionic species transport model seems, due to the no net current hypothesis, not to be able to take into account transport phenomena related to corrosion. Perhaps corrosion-related transport effects can be neglected in environmental applications even if this point is not precisely discussed by Boudreau et al. [7]. For the remainder of the text, only systems with nonzero current density are discussed.

Next, the choice of using the charge conservation equation or the electroneutrality instead of the Gauss's law is addressed. Also, the charge conservation equation and electroneutrality can be used together instead of the Gauss's law. Most electromagnetism systems can be solved with four Maxwell equations and the charge conservation equation [9]. Within the context specified above, there is no obligation to choose the charge conservation equation or Gauss's law in preference. This choice is more a matter of practical justification or related to the nature of the system to be modelled. There is no derivation or hypothesis behind the charge conservation law; it is an observed law of nature [9]. Then, there is no restriction to use the charge conservation law together with species conservation equations instead of Gauss's law. The only restriction is that the constitutive law describing the charge flux should respect the fundamental laws of physics. For example, they should respect the thermodynamic laws for a system at equilibrium (equilibrium in the sense of the thermodynamic definition). There is more freedom in the formulation of the electric flux constitutive law when using the charge conservation law. In the case of Gauss's law, most models [3, 4, 6] use a constant permittivity which could be a questionable simplification in some systems. For example, in salt water, the permittivity dependence on the ion concentrations and electrical potential, in some circumstances [10], cannot be neglected. Another point is that for some systems, transport parameters are sometimes already known [11], but they are not related to permittivity. Relative to Gauss's law, another simplification [3, 4, 6] is to suppose a conservative electric field. This means that the non-conservative part of the electric field is removed [12] in many cases [3, 4, 6], and there is no guarantee of thermodynamic laws compliance without a thermodynamic

analysis. The procedure using the charge conservation equation is different; the potential appears in the constitutive law, and there is no restrictive hypothesis on potential relation to electric field. The potential has to be defined in relation to the current density constitutive law, and this can be done using the same hypotheses of a conservative field or by other theoretical or experimental methods [1, 13] that should respect the thermodynamic laws.

Using the charge conservation law is less strict; the choice of constitutive law for current density is open to any formulation that respects fundamental physico-chemical observations and fundamental laws of nature as mentioned earlier. In conclusion, there is no need to justify the use of conservation of charge in place of the Gauss equation or vice versa; it depends on the system we are analysing and practical issues. There is even a model [5] that combines the use of Gauss's law and charge conservation together with electroneutrality for different parts of the domain to be able to model complex systems.

Subsequently, the choice of using the electroneutrality equation is dependent on the system to solve. For example, using electroneutrality for modelling a capacitive effect near a boundary at the double layer spatial scale is not appropriate [1]. But for a charged surface in a porous media, at a sufficiently large macroscopic spatial scale relative to the pore size, the system will appear electro-neutral. Contrary to the charge conservation equation, the electroneutrality equation is not a fundamental law [1, 9]. In some cases, it is easier to use electroneutrality instead of Gauss's law [1, 4, 14]. In the particular case where the electrical properties of the media are constant, Gauss's law or the charge conservation equation leads to the same Poisson equation under appropriate hypotheses. [1, 9].

There are many models that use species conservation equations together with the charge conservation equation. Some of these models [15–17] indirectly use the electroneutrality idea by solving the binary system with only the electrolyte concentration as the main variable instead of modelling separately the ionic species concentrations. There is also a similar procedure [18] using a change of variable relative to the supporting electrolyte. Another category of models [19–22] uses the electroneutrality condition to remove one of the species conservation equations and one subsequently obtains the removed species concentration using the charge conservation equation with the help of the electroneutrality condition.

The other main approach [23–26] is to solve species conservation equations together with the electroneutrality equation without using Gauss's law or charge conservation equations.

In this paper, we are interested to present two novel methods for electroneutrality implementation in models

that use species conservation equations conjointly to the charge conservation equation without capacitive effect. Numerical solution using finite elements is considered. For the presented methods, there is no need to completely remove a species equation even if the electroneutrality condition is used. Consequently, boundary conditions can be applied on all ionic species and the potential. Being able to have an explicit form for all boundary conditions opens the possibly of easy coupling with other independent variables such as the temperature, magnetic field or any other variable useful at a boundary. Also, a preliminary study [27, 28] of more complex models with a thermodynamic ionic equilibrium equation enforced on an electrochemical system seems to be inconsistent when using electroneutrality methods that remove one species conservation equation.

To conclude this introduction, one can note that different numerical methods have been used to solve electrochemical systems, such as finite element [15, 19, 23], finite difference [6, 16, 24], finite volume [3, 20, 29], pseudo-spectral [5] and lattice Boltzmann [17].

2 Mathematical and numerical models

2.1 General remarks

The proposed methods using the electroneutrality condition are applied to aqueous dilute solutions subject to different electrochemical conditions. The ionic transport model is based on the Nernst–Planck relation. The current density \vec{i} as a function of the solution potential Φ and different ion concentrations c_i for an aqueous solution is therefore defined as [1]:

$$\vec{i} = F \sum_{i=1}^N z_i (-D_i \nabla c_i - z_i c_i u_i F \nabla \Phi) \quad (1)$$

where D_i and u_i are, respectively, the ionic species diffusion coefficient and mobility.

The conservation equations [2a] of the N ionic species are described by the following partial differential equations (PDE):

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \vec{J}_i - s_i R = 0 \quad (2a)$$

$$\vec{J}_i = -D_i \nabla c_i - z_i c_i u_i F \nabla \Phi \quad (2b)$$

where R , in this paper, is the rate of reaction for an electrically balanced reaction only. The stoichiometric coefficients s_i are for the associated reaction. In the following, the rate term is omitted from mathematical derivation for the sake of simplicity, but an example will be given in the

modelling cases used to study the different electroneutrality implementation methods.

In this paper, the capacitive effect is neglected, and thus, the charge conservation equation is defined as follows:

$$\nabla \cdot \vec{i} = \nabla \cdot \left[F \sum_{i=1}^N z_i (-D_i \nabla c_i - z_i c_i u_i F \nabla \Phi) \right] = 0 \quad (3)$$

As discussed in the introduction, electroneutrality is chosen as the complementary equation to be satisfied in the entire domain:

$$\sum_{i=1}^N z_i c_i(\vec{x}, t) = 0 \quad (4)$$

Evidently, the application of Eq. 3 means that, from the analytical point of view, the Eq. 4 would be satisfied without considering boundary conditions [1, 8]. Thus, the problem can be solved using species conservation equations with charge conservation but without the electroneutrality condition. But in this case, the electroneutrality condition is not always sufficiently respected because the electric flux cannot be expressed only in function of the charge density [8] and also due to numerical imprecision when concentrations values are near zero. Thus, to increase the precision relative to the electroneutrality condition, Eq. 3 is added to the system as a constraint.

We thus have a total of $N + 1$ unknown functions N ionic species and the electrical potential and $N + 2$ equations (Eqs. 2a–4). As mentioned in the previous section, Eqs. 2a and 3 are based on the fundamental conservation principles in a continuum media. Equation 4 can be seen as a constraint, which couples together the conservation equations; the solution of species c_i depends on the concentration of all species c_j ($i \neq j$). Based on the discussion in the introduction, Eq. 4 must be satisfied at every point of the domain.

In the following subsections, three approaches are presented to reduce the number of equations to $N + 1$. The first approach is based on the elimination method of one of the conservation equations and the use the electroneutrality. Equation 4 to complete the system as proposed by Ganjoo and Tezduyar [21]. Based on Eq. 4, one can write, assuming that the equation related to the first specie c_1 is eliminated:

$$c_1(\vec{x}, t) = \frac{-1}{z_1} \sum_{i=2}^N (z_i c_i(\vec{x}, t)) \quad (5)$$

Similarly, the second method is based on the construction of the variational formulation using the weighted residual method and Galerkin test functions. Thus, instead of eliminating the partial differential equation as the first method discussed above, all relations linked to Eq. 5 and

its derivatives are explicitly taken into account. Thus, one can easily define all the following equations using the principle of variational calculus and derivation, applied to Eq. 4:

$$\dot{c}_1 = \frac{-1}{z_1} \sum_{i=2}^N (z_i \dot{c}_i) \quad (6)$$

$$\nabla c_1 = \frac{-1}{z_1} \sum_{i=2}^N (z_i \nabla c_i) \quad (7)$$

$$\delta c_1 = \frac{-1}{z_1} \sum_{i=2}^N (z_i \delta c_i) \quad (8)$$

$$\nabla \delta c_1 = \frac{-1}{z_1} \sum_{i=2}^N (z_i \nabla \delta c_i) \quad (9)$$

where δc_i corresponds to Galerkin test functions or the variation of c_i in the framework of variational calculus [30, 31]. All those relations will be used to replace functions c_1 and δc_1 and their derivatives inside the variational integral equation.

The third method is based on the fact that Eq. 4 can be seen as a constraint. Thus, using Lagrange multiplier method, this constraint will be added to the system of equations to be solved. Thus, all the conservation equations of chemical species involved will be solved without any modification, as required for the second method.

The following equations are defined as a basis for developing all the methods presented in this paper. As presented in the “Appendix,” using the weighted residual method, one can write:

$$W = W_c + W_\Phi = 0 \quad (10)$$

$$W_c = \int_V \sum_{i=1}^N \left[\delta c_i \left(\frac{\partial c_i}{\partial t} + \nabla \cdot \vec{J}_i \right) \right] dV \quad (11)$$

$$W_\Phi = \int \delta \Phi \nabla \cdot \vec{i} dV \quad (12)$$

where $\delta \Phi$ is the test function for the electrical problem. To be able to use lower order finite element method and to introduce Neumann boundary conditions, the weak form of Eq. 10 is necessary [30, 31]:

$$W_c = \sum_{i=1}^N \left[\int \delta c_i \frac{\partial c_i}{\partial t} dV - \int \nabla \delta c_i \cdot \vec{J}_i dV + \oint \delta c_i \vec{J}_i \cdot d\vec{A} \right] \quad (13)$$

$$W_\Phi = - \int \nabla(\delta \Phi) \cdot \vec{i} dV + \oint \delta \Phi \vec{i} \cdot d\vec{A} = 0 \quad (14)$$

where $\vec{J}_i = \vec{J}_i \cdot \vec{n}$ is the Neumann boundary conditions for each species on boundary Γ_N and $\vec{i} = \vec{i} \cdot \vec{n}$ is the Neumann boundary condition for the current density on boundary Γ_N .

2.2 Equation elimination method (EEM)

The easiest way to solve Eqs. 10 with 13 and 14 is to remove one of the species conservation equations combined with the use of the electroneutrality condition (Eq. 5) to retrieve the value of the first species which was eliminated. Then, equations to solve are as follows:

$$W_c = \sum_{i=2}^N \left[\int \delta c_i \frac{\partial c_i}{\partial t} dV - \int \nabla(\delta c_i) \cdot \vec{J}_i dV + \oint \delta c_i \vec{J}_i dA \right] \quad (15)$$

$$W_\phi = - \int \nabla \delta \Phi \cdot \vec{i} dV + \oint \delta \Phi \vec{i} dA = 0 \quad (16)$$

where \vec{i} defined in Eq. 1 is redefined as follows using Eqs. 5 and 7:

$$\vec{i} = F \left(D_1 \sum_{i=2}^N (z_i \nabla c_i) - \sum_{i=2}^N (z_i D_i \nabla c_i) \right) + F^2 \nabla \Phi \left(z_1 u_1 \sum_{i=2}^N (z_i c_i) - \sum_{i=2}^N (z_i^2 c_i u_i) \right) \quad (17)$$

Subsequently, the equation system to solve combines the Eq. 16 with the current density defined in Eq. 17 and the $N - 1$ remaining species conservation equations defined in Eq. 15. Finally, the species concentration c_1 is computed a posteriori using the electroneutrality Eq. 5.

It is important to remember that, with this method, no explicit boundary condition can be applied to chemical species c_1 . The first method is called EEM. The Nernst–Planck transient module of COMSOL 3.5a seems to use a similar method [32] (The authors refer to the COMSOL guide, but the Nernst–Planck transient module is not discussed in detail there).

It is worth mentioning that some systems have a limited choice for species elimination. For example, the system of molten salt NaF–AlF₃–Al₂O₃ where aluminium discharge occurs at the surface of porous carbon cathode. In the studying context of Hall–Héroult cell processes, the simple system is frequently used [33, 34]. As the kinetic of the ionic complexation reactions are unknown [33], one of the main hypotheses is to consider them sufficiently fast to be at equilibrium. Then, the only available ions are those not involved in an ionic complexation reaction or the alumina dissolution. Then, for this system, there are only three available ions: Na¹⁺, F^{1−} and AlF₄^{1−} (the choice can be slightly different: AlF₆^{3−} instead of AlF₄^{1−}, but only three are remaining). The boundary condition for the aluminium discharge involves the fluoride ion and at least an aluminofluoride ion (or oxyaluminofluoride). It means that the only ion available for elimination is Na¹⁺. But, in the context of cathode degradation study and modelling

[33, 34], there is a need to apply boundary conditions on Na¹⁺ to assess the non-equilibrium metallic sodium formation and the sodium intercalation process in anthracitic carbon of the ramming paste.

2.3 Consistent equation elimination method (CEEM)

The second method is an elimination method taking account of all dependencies between the electroneutrality equation and the other equations. We use the Eqs. 5–9 to replace all quantities related to the specie c_1 , its variation (test functions) and all derivatives of these two quantities. In this way, we can define explicitly the dependency between all quantities c_i .

To be able to write the correct variational formulation using all dependencies between the species, the weak form related to c_i , W_c defined in Eq. 13, is written as follows:

$$W_c = W_c^1 + W_c^i \quad (18)$$

$$W_c^1 = \int \delta c_1 \frac{\partial c_1}{\partial t} dV - \int \nabla \delta c_1 \cdot (-D_1 \nabla c_1 - z_1 c_1 u_1 F \nabla \Phi) dV + \oint \delta c_1 \vec{J}_1 dA \quad (19)$$

$$W_c^i = \sum_{i=2}^N \left[\int \delta c_i \frac{\partial c_i}{\partial t} dV - \int \nabla \delta c_i \cdot \vec{J}_i dV + \oint \delta c_i \vec{J}_i dA \right] \quad (20)$$

Then, by substituting Eqs. 5–9 in Eq. 19, it can be shown that the final variational form W_c is defined as follows (see “Appendix”):

$$W_c = \sum_{k=1}^4 W_c^k \quad (21)$$

$$W_c^1 = \sum_{i=2}^N \left[\int \delta c_i \left(\frac{\partial c_i}{\partial t} + \frac{z_i}{z_1^2} \sum_{j=2}^N z_j \frac{\partial c_j}{\partial t} \right) dV \right] \quad (22)$$

$$W_c^2 = \sum_{i=2}^N \left[\int \nabla \delta c_i \cdot \left(D_i \nabla c_i + \frac{z_i D_1}{z_1^2} \sum_{j=2}^N z_j \nabla c_j \right) dV \right] \quad (23)$$

$$W_c^3 = \sum_{i=2}^N \left[\int \nabla \delta c_i \cdot \left[z_i F \nabla \Phi \left(c_i u_i + \frac{u_1}{z_1} \sum_{j=2}^N z_j c_j \right) \right] dV \right] \quad (24)$$

$$W_c^4 = \sum_{i=2}^N \left[\oint \delta c_i \left(\vec{J}_i - \frac{z_i}{z_1} \vec{J}_1 \right) dA \right] \quad (25)$$

The variational formulation for W_ϕ is the same as the one defined in the previous section.

We can observe from Eqs. (22)–(25) that all physical parameters relied to the diffusion and migration of the

species c_1 are included in the variation formulation Eq. 21. Also, as we can see it at Eq. 25, it is possible to apply a Neumann boundary (flux) condition on Γ_N for the species c_1 . For Dirichlet boundary condition on Γ_D , due to the fact that the electroneutrality must be satisfied on this boundary, it is clear that:

$$c_1|_{\Gamma_D} = \frac{-1}{z_1} \sum_{i=2}^N (z_i c_i|_{\Gamma_D})$$

Using the following definitions:

$$\begin{aligned} \bar{J}_i^c &= - \left[\left(\frac{D_1}{z_1^2} \sum_{j=2}^N z_j \nabla c_j \right) + F \nabla \Phi \frac{u_1}{z_1} \sum_{j=2}^N (z_j c_j) \right] \\ \bar{J}_1^c &= - \frac{1}{z_1} \bar{J}_1 \end{aligned} \quad (26)$$

and Eqs. 16 and 21–25, we can write:

$$\begin{aligned} W &= \sum_{i=2}^N \left[\int \delta c_i \left(\frac{\partial c_i}{\partial t} + \frac{z_i}{z_1^2} \sum_{j=2}^N z_j \frac{\partial c_j}{\partial t} \right) dV \right. \\ &\quad \left. - \int \nabla(\delta c_i) (\bar{J}_i + z_i \bar{J}_i^c) dV + \oint \delta c_i (\bar{J}_i + z_i \bar{J}_1^c) dA \right] \\ &\quad - \int \nabla(\delta \Phi) \cdot \vec{i} dV + \oint \delta \Phi \vec{i} dA = 0 \end{aligned} \quad (27)$$

In the case of CEEM, as EEM, the current density must be defined by using Eq. 17. It is easy to show using gradient and divergence theorem [35], applied to Eq. 27:

$$\begin{aligned} W &= \sum_{i=2}^N \left[\int \delta c_i \left(\frac{\partial c_i}{\partial t} + \frac{z_i}{z_1^2} \sum_{j=2}^N z_j \frac{\partial c_j}{\partial t} \right) dV \right. \\ &\quad \left. + \int \delta c_i \nabla \cdot (\bar{J}_i + z_i \bar{J}_i^c) dV \right] \\ &\quad + \sum_{i=2}^N \left[- \oint \delta c_i (\bar{J}_i + z_i \bar{J}_1^c) dA + \oint \delta c_i (\bar{J}_i + z_i \bar{J}_1^c) dA \right] \\ &\quad + \int (\delta \Phi) \nabla \cdot \vec{i} dV - \oint \delta \Phi \vec{i} dA + \oint \delta \Phi \vec{i} dA \\ &= \sum_{i=2}^N \left[\int \delta c_i \left(\frac{\partial c_i}{\partial t} + \frac{z_i}{z_1^2} \sum_{j=2}^N z_j \frac{\partial c_j}{\partial t} + \nabla \cdot (\bar{J}_i + z_i \bar{J}_i^c) \right) dV \right] \\ &\quad + \int \delta \Phi \nabla \cdot \vec{i} dV = 0 \end{aligned} \quad (28)$$

This last equation must be zero regardless of the value of test functions δc_i and $\delta \Phi$ permitting to write the following PDEs ($N - 1$ species and one for the charge conservation):

$$\begin{aligned} \left(\frac{\partial c_i}{\partial t} + \nabla \cdot \bar{J}_i \right) + z_i \left(\frac{1}{z_1^2} \sum_{j=2}^N \left(z_j \frac{\partial c_j}{\partial t} \right) \right. \\ \left. + \nabla \cdot (\bar{J}_i^c) \right) = 0 \quad (i \geq 2) \quad \nabla \cdot \vec{i} = 0 \end{aligned} \quad (29)$$

We can observe the strong coupling between all species due to the electroneutrality condition. Eqs. 26 and 29 show clearly the coupling between the flux of the species c_i and the gradient of all the other species c_j and the mobility parameter u_j and concentration c_j . It appears that the accumulation term for c_i is also a function of the accumulation terms $\frac{\partial c_j}{\partial t}$.

PDEs 29 contain two parts: the part already defined in Eq. 2a and an additional part coming from the rigorous application of the electroneutrality condition. One may observe also that de PDEs corresponding to the balance of species c_2 to c_N , that there exist two types of flux: the classical flux of the corresponding species and a corrective flux that appears due to the fact that the electroneutrality condition must be satisfied. The additional terms in Eq. 29 are equivalent to a sink or a source, and there is a similarity with what Sarkar and Aquino [36] have proposed as a physical signification behind their mathematical approach. It can be shown that Eq. 29 implicitly satisfies the conservation equation for the eliminated species. This is easily shown by substitution of the species c_1 definition by using Eqs. 6 and 7:

$$\begin{aligned} \left(\frac{\partial c_i}{\partial t} + \nabla \cdot \bar{J}_i \right) + z_i \left(\frac{1}{z_1^2} \sum_{j=2}^N \left(z_j \frac{\partial c_j}{\partial t} \right) + \nabla \cdot (\bar{J}_i^c) \right) \\ = \left(\frac{\partial c_i}{\partial t} + \nabla \cdot \bar{J}_i \right) - \frac{z_i}{z_1} \left(\frac{\partial c_1}{\partial t} + \nabla \cdot \bar{J}_1 \right) = 0 \quad (i \geq 2) \\ \nabla \cdot \vec{i} \end{aligned} \quad (30)$$

Then, by continuity, the last term of Eq. 30 disappears and the CEEM method becomes formally like the EEM method, but in practice, they are numerically different as the last term of Eq. 30 is evaluated for the CEEM method. Furthermore, in the case of EEM method, the transport parameters related to the eliminated species are taken in account only in the charge conservation equation. It will be seen in the next section that some links also exist between this method (CEEM) and the Lagrange multiplier method (LMM).

The major difficulty with CEEM method is the complexity of writing the final form to be solved. Of course, the final variational formulation depends on the species eliminated using the electroneutrality equation, but the global form stays the same. Also, the final form can be dependant upon the constitutive law used for defining the current density or other terms like a source or sink.

2.4 Lagrange multiplier method (LMM)

The last method is based on the Lagrange multipliers method [30, 31]. As discussed in the introduction, the idea

behind this method is that the electroneutrality should be seen as a constraint associated with the scale of the system and not as a fundamental equation. A constraint, by the Lagrange multiplier method, can be applied to a system of equations to be solved by finite element method using a variational integral form. It is worth mentioning that using the Lagrange multiplier method introduces a supplementary variable to be solved for over the entire domain where the constraint is applied. The application of the electroneutrality condition as a constraint using the Lagrange multiplier generates a functional of the following form:

$$\Pi^*(c_i, \Phi, \lambda) = \Pi(c_i, \Phi) + \int \lambda(\vec{x}, t) \left(\sum_{i=1}^N c_i z_i \right) dV \quad (32)$$

To obtain the variational formulation to be used for solving by finite element method, the first variation of the functional defined in 32 must be performed [30, 31]:

$$\begin{aligned} \delta \Pi^*(c_i, \Phi, \lambda) = & \delta \Pi(c_i, \Phi) + \int \delta \lambda \left(\sum_{i=1}^N c_i z_i \right) dV \\ & + \sum_{i=1}^N \int \lambda z_i \delta c_i dV = 0 \end{aligned} \quad (33)$$

The last two terms associated with the electroneutrality constraint of Eq. 33 are directly added to variational formulation defined in Eqs. 10, 13 and 14 corresponding to $\delta \Pi(c_i, \Phi)$. The final variational formulation to be solved by finite element method is written as follows:

$$\begin{aligned} W = & \sum_{i=1}^N \left[\int \delta c_i \left(\frac{\partial c_i}{\partial t} + \lambda z_i \right) \right. \\ & \left. - \nabla \delta c_i \cdot (-D_i \nabla c_i - z_i c_i u_i F \nabla \Phi) dV \right] + \int \delta \lambda \left(\sum_{i=1}^N z_i c_i \right) dV \\ & + \sum_{i=1}^N \oint \delta c_i \bar{J}_i dA + W_\Phi = 0 \end{aligned} \quad (34)$$

where it is easy to demonstrate that the PDEs relative to Eq. 34 are the same as defined by Eqs. 15 and 16 when the electroneutrality constraint is sufficiently numerically enforced:

$$\begin{aligned} & \sum_{i=1}^N \left[\int \lambda (\delta c_i z_i) dV \right] + \int \delta \lambda \left(\sum_{i=1}^N z_i c_i \right) dV \\ & = \int \lambda \delta \left(\sum_{i=1}^N c_i z_i \right) dV + \int \delta \lambda \left(\sum_{i=1}^N z_i c_i \right) dV \\ & = \int \lambda \delta(0) dV + \int \delta \lambda(0) dV \end{aligned} \quad (35)$$

Also one may observe that here again a source/sink term appears in Eq. 34 similarly to Eqs. 29 or 30 (CEEM). While it is not obvious that CEEM and LMM are similar,

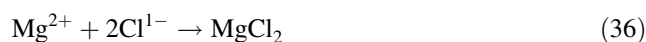
in the “Appendix,” it is shown that method CEEM and LMM are equivalent analytically. In the next section, based on finite element simulation, one can demonstrate that these two methods give the same results.

Here again, one can observe a strong coupling of all equations linked via the Lagrange multiplier. It must be noted that the Lagrange multiplier is a function and its value varies in time and space. This function will be discretized using a finite element method.

In the modelling cases chosen hereafter, all electroneutrality implementation methods should give the same results whatever the eliminated species conservation equation or non-explicitly applied boundary conditions because of the enforced electroneutrality equation, the charge conservation equation used without a capacitive term and the use of electrically balanced chemical reactions. This is a fact independent of the solution method and the flux constitutive law definition, but it is related to the chosen physical model and its associated hypotheses mentioned previously. The last comment can be shown by summing the species conservation equations multiplied by the associated species charge number [1].

3 Modelling cases

A dilute aqueous solution of different ions was defined as a test case to compare the three electroneutrality implementation methods. The aqueous solution is constituted of ionized NaCl and MgBr₂. To avoid the modelling of the acid–base equilibrium, the ions H¹⁺ and OH^{1−} are not included in the model. Its inclusion could introduce stronger coupling between species and nonlinearity that could bring unnecessary difficulties for the numerical comparisons between the different electroneutrality implementation methods. Four different kinds of problems were tested for the same aqueous solution. The first case A is a conduction problem with Neumann boundary conditions only. There is an influx of cationic species at a boundary and an anionic influx at the other boundary. The case B is a half cell with consumption of the anion Cl^{1−} at a boundary impermeable to other species and a Dirichlet boundary condition for all species at the other boundary. The case C is the same as case B except that a fictive reaction removing MgCl₂ was added in the central third of the domain acting as a sink:



A simple nonlinear rate law for reaction (36) was formulated as follows:

$$s_i R = s_i k c_{\text{Mg}^{2+}} c_{\text{Cl}^{1-}}^2 \quad (37)$$

The constant s_i is the stoichiometry of the species i for the reaction rate R . The kinetic constant k was defined negative

to define a sink term. The adding of a sink term brings supplementary terms in the CEEM method if the eliminated species is involved in the reaction:

$$-\int \delta c_1 s_1 R dV = -\int \left(-\frac{1}{z_1} \sum_{i=2}^N z_i \delta c_i \right) s_1 R dV \\ = \sum_{i=2}^N \int s_1 R \frac{z_i}{z_1} \delta c_i dV \quad (38)$$

By substitution of the rate Eq. 37 into Eq. 38, one may obtain the term to be added to other species conservation equations. Notice that the supplementary term defined in Eq. 38 has the same form of other terms in Eq. 30 except for the presence of the stoichiometric coefficient. The other methods are not affected by the addition of a rate term except for the presence of the sink term in the conservation equation for chloride and magnesium ions. There is no modification to charge conservation because the reaction is electrically balanced.

The case D is the same problem as case B except that instead of a forced current and an imposed chloride flux on the boundary, a Butler–Volmer kinetic is used as a boundary condition for the current density and chloride ion flux:

$$i_{\text{Butler-Volmer}} = i_0 \left[e^{\left(\frac{z_a F}{RT} \eta_s \right)} - e^{\left(-\frac{z_c F}{RT} \eta_s \right)} \right] \quad (39)$$

The current density is function of surface overvoltage η_s and parameters like exchange current density i_0 and apparent cathodic and anodic transfer coefficients α . The overvoltage is defined as follows:

$$\eta_s = \Phi_s - \Phi - U \quad (40)$$

where U and Φ_s are, respectively, the equilibrium and the electrode surface potential.

Le last case E is more complex and different from the other cases because it includes an enforced ionic equilibrium equation. The aqueous dilute solution is constituted of ionized NaCl, FeCl₂ and Na₄Y where Y is for EDTA. As with the other cases, the modelling of the acid–base equilibrium is avoided for simplification purposes. The ionic equilibrium chosen is a complexation reaction of ferrous ion and EDTA:



$$K = \frac{c_{\text{FeY}^{2-}}}{c_{\text{Fe}^{2+}} c_{\text{Y}^{4-}}} \quad (42)$$

The problem is in part fictive because of the removal of the acid–base equilibrium that plays a role on EDTA complexation properties and the equilibrium constant chosen (see Table 4) is much lower than the measured ones [37]. On the opposite, the diffusion coefficients for species implied in equilibrium (41) are of the same order of

Table 1 Values for parameters of cases A–D

Parameters	Values
j_{boundary}	$5 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$
$j_{\text{Cl}^{1-}}$	$-1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$
c_{initial}	0.01 mol m^{-3}
$D_{\text{Na}^{1+}}$ [11]	$1.334 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
$D_{\text{Mg}^{2+}}$ [11]	$0.706 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
$D_{\text{Cl}^{1-}}$ [11]	$2.032 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
$D_{\text{Br}^{1-}}$ [11]	$2.080 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
Φ_{initial}	0 V
λ_{initial}	1
L	1 mm
T	298.15 K
k	$500 \left[H\left(x - \frac{L}{3}\right) - H\left(x - \frac{2L}{3}\right) \right]$ H is for Heaviside functions
i_0	0.005 A m^{-2}
α_a	1.5
α_c	0.5
Φ_s	0.05 V
U	0 V
u_i	$\frac{D_i}{RT}$

magnitude of those measured [38]. The reaction (41) is supposed to be sufficiently fast relative to transport phenomena to be considered almost at equilibrium. The ionic equilibrium Eq. 42 is then enforced by using a direct substitution approach which is method part of the global implicit group used in the transport–reaction modelling field of research [39, 40]. For the equilibrium implementation, the species eliminated is FeY^{2−} except in the case where the ion FeY^{2−} is selected for elimination with the electroneutrality equation. In this case, the alternative ion chosen is Y^{4−}. First, the procedure of elimination proceeds by substitution of Eq. 42 in all equations to eliminate the chosen species concentration variable (here, $c_{\text{FeY}^{2-}}$ or $c_{\text{Y}^{4-}}$). As a second step, Eqs. 2a and 2b for the chosen species to be eliminated are used to reformulate the equilibrium-associated source term (here, as an example, FeY^{2−}):

$$R = \frac{1}{s_{\text{FeY}^{2-}}} \left[\frac{\partial c_{\text{FeY}^{2-}}}{\partial t} + \nabla \cdot \vec{J}_{\text{FeY}^{2-}} \right] \\ c_{\text{FeY}^{2-}} = f(c_{\text{Fe}^{2+}}, c_{\text{Y}^{4-}}) \quad \vec{J}_{\text{FeY}^{2-}} = f(c_{\text{Fe}^{2+}}, c_{\text{Y}^{4-}}, \Phi) \quad (43)$$

Subsequently, the source term R is substituted in species conservation equations involved in the reaction (41). To complete case E, an influx of Fe²⁺ is applied at a boundary impermeable to other species and a Dirichlet boundary condition for all species is imposed at the other boundary.

Table 2 Initial and boundary conditions for the multiionic conduction problem

Case A	Boundary	
$c_{\text{Na}^{1+}}(x, 0) = c_{\text{initial}}$	$-\vec{n} \cdot \vec{J}_{\text{Na}^{1+}}(0, t) = j_{\text{boundary}}$	$-\vec{n} \cdot \vec{J}_{\text{Na}^{1+}}(L, t) = 0$
$c_{\text{Mg}^{2+}}(x, 0) = \frac{c_{\text{initial}}}{2}$	$-\vec{n} \cdot \vec{J}_{\text{Mg}^{2+}}(0, t) = \frac{j_{\text{boundary}}}{2}$	$-\vec{n} \cdot \vec{J}_{\text{Mg}^{2+}}(L, t) = 0$
$c_{\text{Cl}^{1-}}(x, 0) = c_{\text{initial}}$	$-\vec{n} \cdot \vec{J}_{\text{Cl}^{1-}}(0, t) = 0$	$-\vec{n} \cdot \vec{J}_{\text{Cl}^{1-}}(L, t) = j_{\text{boundary}}$
$c_{\text{Br}^{1-}}(x, 0) = c_{\text{initial}}$	$-\vec{n} \cdot \vec{J}_{\text{Br}^{1-}}(0, t) = 0$	$-\vec{n} \cdot \vec{J}_{\text{Br}^{1-}}(L, t) = j_{\text{boundary}}$
$\Phi(x, 0) = \Phi_{\text{initial}}$	$-\vec{n} \cdot \vec{i}(0, t) = F\left(z_{\text{Na}^{1+}} + \frac{z_{\text{Mg}^{2+}}}{2}\right)j_{\text{boundary}}$	$-\vec{n} \cdot \vec{i}(L, t) = F(z_{\text{Cl}^{1-}} + z_{\text{Br}^{1-}})j_{\text{boundary}}$
$\lambda(x, 0) = \lambda_{\text{initial}}$		

Table 3 Initial and boundary conditions for the half cell problems

Cases B, C, D	Boundary	
$c_{\text{Na}^{1+}}(x, 0) = c_{\text{initial}}$	$-\vec{n} \cdot \vec{J}_{\text{Na}^{1+}}(0, t) = 0$	$c_{\text{Na}^{1+}}(L, t) = c_{\text{initial}}$
$c_{\text{Mg}^{2+}}(x, 0) = \frac{c_{\text{initial}}}{2}$	$-\vec{n} \cdot \vec{J}_{\text{Mg}^{2+}}(0, t) = 0$	$c_{\text{Mg}^{2+}}(L, t) = \frac{c_{\text{initial}}}{2}$
$c_{\text{Cl}^{1-}}(x, 0) = c_{\text{initial}}$	$-\vec{n} \cdot \vec{J}_{\text{Br}^{1-}}(0, t) = 0$	$c_{\text{Cl}^{1-}}(L, t) = c_{\text{initial}}$
$c_{\text{Br}^{1-}}(x, 0) = c_{\text{initial}}$		$c_{\text{Br}^{1-}}(L, t) = c_{\text{initial}}$
$\Phi(x, 0) = \Phi_{\text{initial}}$		$\Phi(L, t) = \Phi_{\text{initial}}$
$\lambda(x, 0) = \lambda_{\text{initial}}$		$\lambda(L, t) = \lambda_{\text{initial}}$

Case B, C	Boundary
	$-\vec{n} \cdot \vec{J}_{\text{Cl}^{1-}}(0, t) = j_{\text{Cl}^{1-}}$
	$-\vec{n} \cdot \vec{i}(0, t) = Fz_{\text{Cl}^{1-}}j_{\text{Cl}^{1-}}$

Case D	Boundary
	$-\vec{n} \cdot \vec{J}_{\text{Cl}^{1-}}(0, t) = \frac{i_{\text{Butler-Volmer}}}{z_{\text{Cl}^{1-}}F}$
	$-\vec{n} \cdot \vec{i}(0, t) = i_{\text{Butler-Volmer}}$

Table 4 Values for parameters of case E

Parameters	Values
$D_{\text{Fe}^{2+}}$	$0.719 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
$D_{\text{Y}^{4-}}$	$0.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
$D_{\text{FeY}^{2-}}$	$0.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
K	100
\bar{i}	0.02 A m^{-2}
Φ_{initial}	0 V
λ_{initial}	1

Solution composition prior to ionic dissociation and equilibrium

$c_{\text{NaCl}}(x, 0)$	0.01 mol m^{-3}
$c_{\text{FeCl}_2}(x, 0)$	0.001 mol m^{-3}
$c_{\text{Na}_4\text{Y}}(x, 0)$	0.001 mol m^{-3}

Solution composition for initial conditions after dissolution and equilibrium

$c_{\text{Na}^{1+}}^{\text{equil}}$	0.014 mol m^{-3}
$c_{\text{Cl}^{1-}}^{\text{equil}}$	0.012 mol m^{-3}
$c_{\text{Fe}^{2+}}^{\text{equil}}$	$\approx 9.160798 \times 10^{-4} \text{ mol m}^{-3}$
$c_{\text{Y}^{4-}}^{\text{equil}}$	$\approx 9.160798 \times 10^{-4} \text{ mol m}^{-3}$

Table 5 Initial and boundary conditions for the ionic conduction problem including an ionic equilibrium

Case E	Boundary	
$c_{\text{Na}^{1+}}(x, 0) = c_{\text{Na}^{1+}}^{\text{equil}}$	$-\vec{n} \cdot \vec{J}_{\text{Na}^{1+}}(0, t) = 0$	$c_{\text{Na}^{1+}}(L, t) = c_{\text{Na}^{1+}}^{\text{equil}}$
$c_{\text{Cl}^{1-}}(x, 0) = c_{\text{Cl}^{1-}}^{\text{equil}}$	$-\vec{n} \cdot \vec{J}_{\text{Cl}^{1-}}(0, t) = 0$	$c_{\text{Cl}^{1-}}(L, t) = c_{\text{Cl}^{1-}}^{\text{equil}}$
$c_{\text{Fe}^{2+}}(x, 0) = c_{\text{Fe}^{2+}}^{\text{equil}}$	$-\vec{n} \cdot \vec{J}_{\text{Fe}^{2+}}(0, t) = \frac{\bar{i}}{2F}$	$c_{\text{Fe}^{2+}}(L, t) = c_{\text{Fe}^{2+}}^{\text{equil}}$
$c_{\text{Y}^{4-}}(x, 0) = c_{\text{Y}^{4-}}^{\text{equil}}$	$-\vec{n} \cdot \vec{J}_{\text{Y}^{4-}}(0, t) = 0$	$c_{\text{Y}^{4-}}(L, t) = c_{\text{Y}^{4-}}^{\text{equil}}$
$\Phi(x, 0) = \Phi_{\text{initial}}$	$-\vec{n} \cdot \vec{i}(0, t) = \bar{i}$	$\Phi(L, t) = \Phi_{\text{initial}}$
$\lambda(x, 0) = \lambda_{\text{initial}}$		$\lambda(L, t) = \lambda_{\text{initial}}$

Table 6 COMSOL 3.5a solver parameters for the different cases

Parameter	Value or option
Application mode	PDE general form
Solver (backward differentiation formula)	BDF maximum order of 5
Time step taken by the solver	Free
Constant initialization of DAE systems	Backward Euler
Error estimation strategy	Include algebraic
Relative tolerance	0.01
Absolute tolerance	0.001
Direct linear system solver	UMFPACK
Row equilibration	Activated
Scaling	Automatic
Null-space function	Automatic
Constraint handling method	Elimination
Nonlinear solver	Automatic
Element maximum size	1×10^{-7}
Element type	Cases A–D: Linear Case E: Quadratic

In all cases, convection and thermal effects have not been taken into account. All models are transient and one-dimensional. The domain size L is 1 mm. All parameters values are shown in Tables 1 and 4. The parameters without references were chosen to obtain a consistent

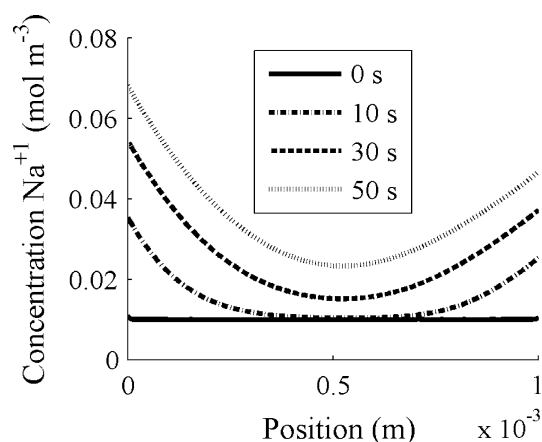


Fig. 1 Concentration of Na^{1+} as a function of time and position for case A

model. The mobility coefficients are obtained from diffusion coefficients using the Nernst–Einstein equation.

The different initial and boundary conditions for each modelling case are presented in Tables 2, 3 and 5. The normal \vec{n} at boundaries are pointing outside the domain. It is to be remembered that case C is the same as case B except that a sink term was added. In the same way, the case D is identical to case B except that the boundary conditions on current density and on the chloride ion value have been modified (Table 3).

The transient Nernst–Planck application mode of COMSOL 3.5a was also used to compare the results to the ones obtained from proposed methods. All other simulations were solved in the COMSOL 3.5a PDE general form mode. The COMSOL 3.5a solver parameters were the same for all methods and are presented in Table 6. The mesh contains 10,000 two-node elements for all solving methods. The simulations were stopped when the concentration of one the ionic species reaches nearly zero.

For the CEEM and EEM, a species has to be chosen in order to remove the associated conservation equation. In the procedure of the Nernst–Planck module of COMSOL 3.5a, a species also needs to be chosen for removal from the system of equations. Thus, no explicit boundary conditions can be applied on the eliminated species as it is for the EEM method. Then, all species were eliminated one after the other, to compare the effect of the selected eliminated species on the solution. All possible options of elimination were tested and gave the same results except for case E, as presented in the next section. For the special case E, it is not possible in the Nernst–Planck module of COMSOL 3.5a to eliminate ion for electroneutrality implementation that occur in the equilibrium reaction (41). This is because the Nernst–Planck module only solve in function of the dependent variables defined for the

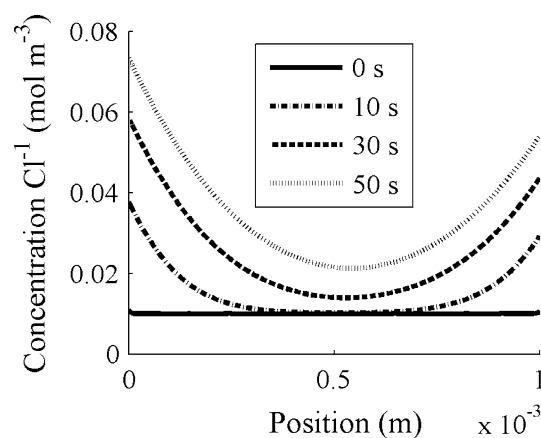


Fig. 2 Concentration of Cl^{1-} as a function of time and position for case A

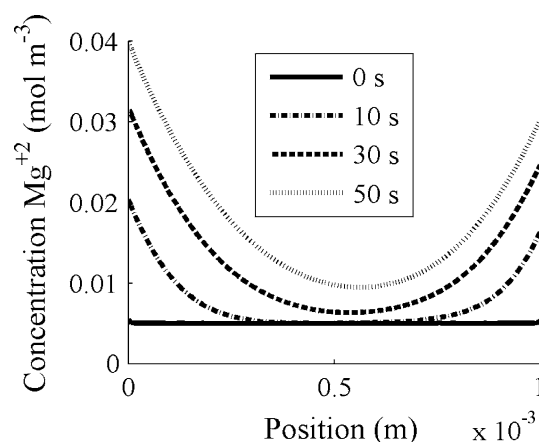


Fig. 3 Concentration of Mg^{2+} as a function of time and position for case A

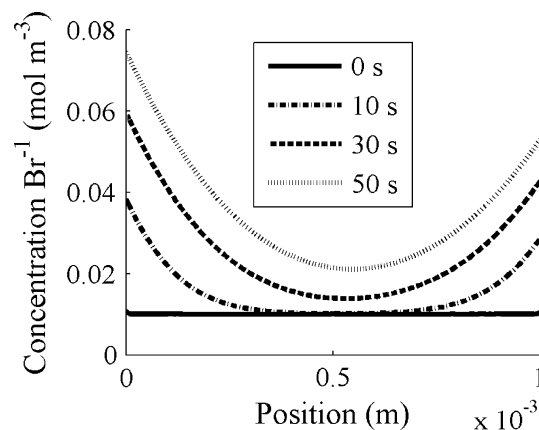


Fig. 4 Concentration of Br^{1-} as a function of time and position for case A

application mode which exclude the one used for electroneutrality and the one used to redefine the source term as was done with Eq. 43.

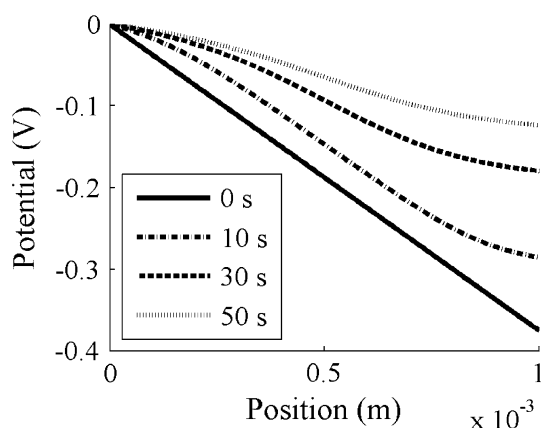


Fig. 5 Solution potential as a function of time and position for case A referred to an arbitrary fixed potential of 0 V at boundary $x = 0$

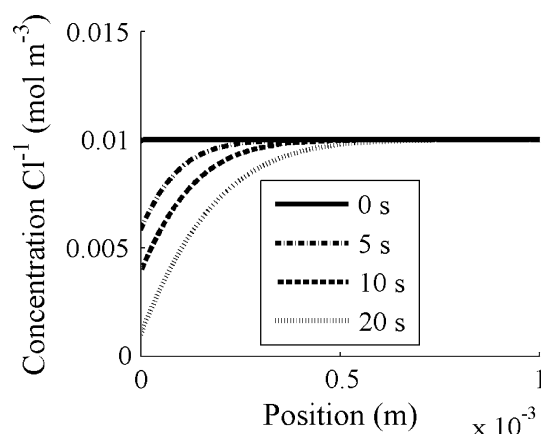


Fig. 7 Concentration of Cl^{1-} as a function of time and position for case B

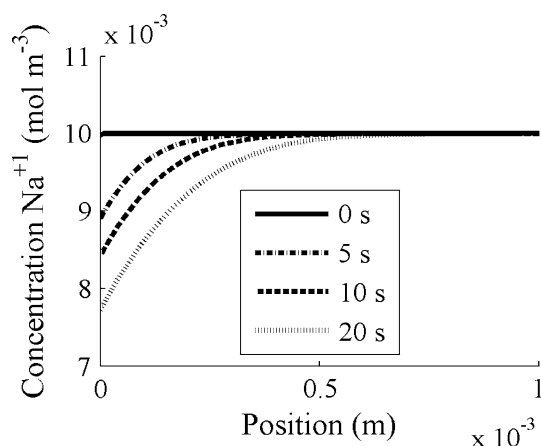


Fig. 6 Concentration of Na^{1+} as a function of time and position for case B

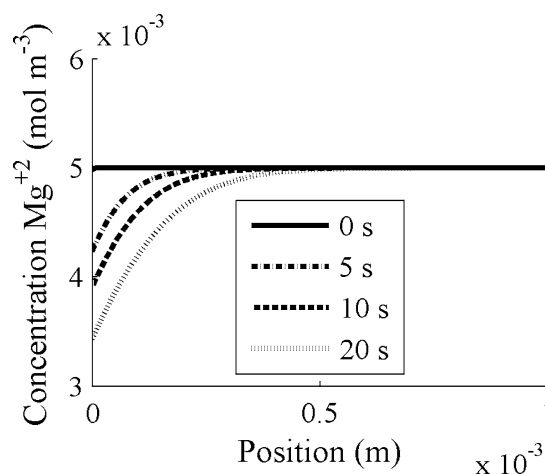


Fig. 8 Concentration of Mg^{2+} as a function of time and position for case B

4 Results and discussions

4.1 Case A

Figures 1, 2, 3 and 4 show the concentration of the different ions at different times. All methods gave the same results. The ionic concentrations rise near the boundary where there is a fixed influx of ionic species and consequently a fixed current density. Oppositely charged species move to neutralize the boundary ionic influx. The curves are not perfectly symmetric because the anions' transport properties are larger than the cationic ones. Even if Mg^{2+} is of higher charge, its higher neutralization capacity is not sufficient to compensate its lower transport parameters because the Nernst–Einstein relation was used to obtain the ionic mobilities ($2D_{\text{Mg}^{2+}} < D_{\text{Cl}^{1-}} < D_{\text{Br}^{1-}}$).

The Fig. 5 shows the aqueous solution potential profile. The slope is steeper where the total ionic

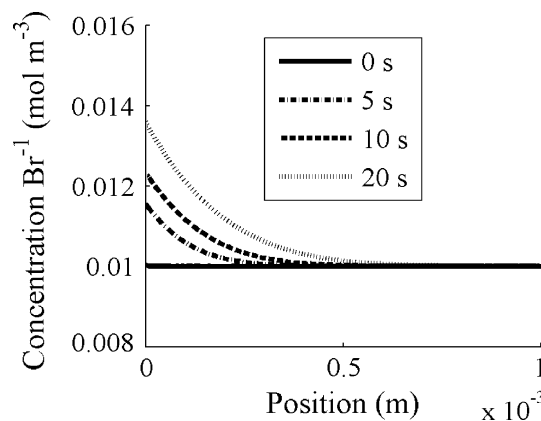


Fig. 9 Concentration of Br^{1-} as a function of time and position for case B

concentration is lower. The curve is not fully linear because of non-uniform ionic concentration distribution.

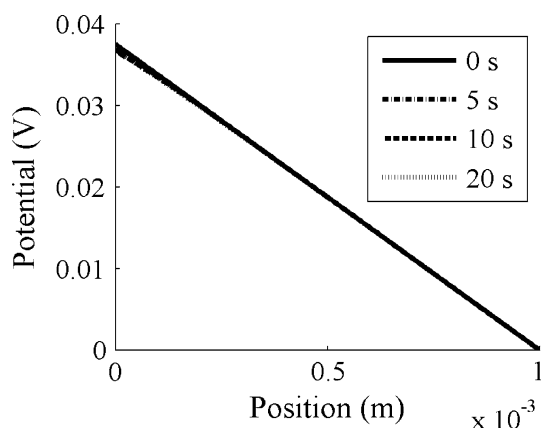


Fig. 10 Solution potential as a function of time and position for case B referred to a fixed potential of 0 V as a Dirichlet boundary condition at $x = L$

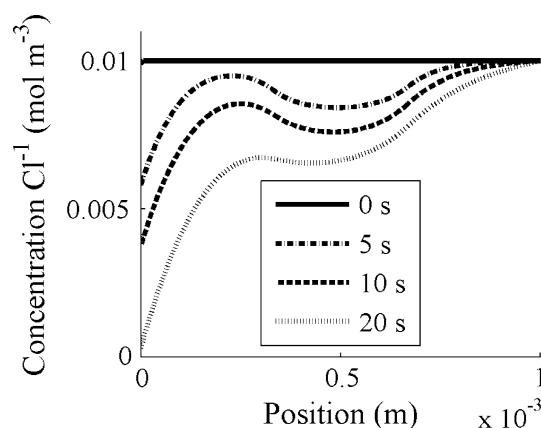


Fig. 12 Concentration of Cl^{1-} as a function of time and position for case C

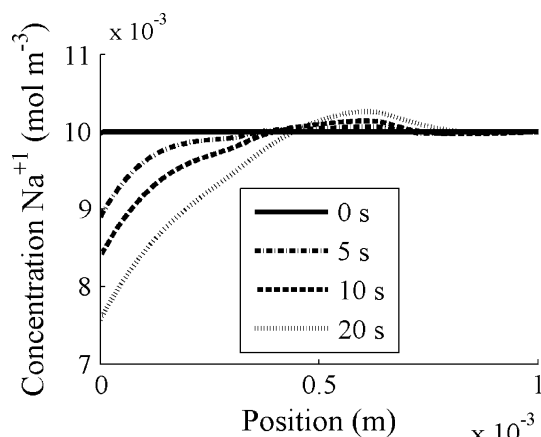


Fig. 11 Concentration of Na^{1+} as a function of time and position for case C

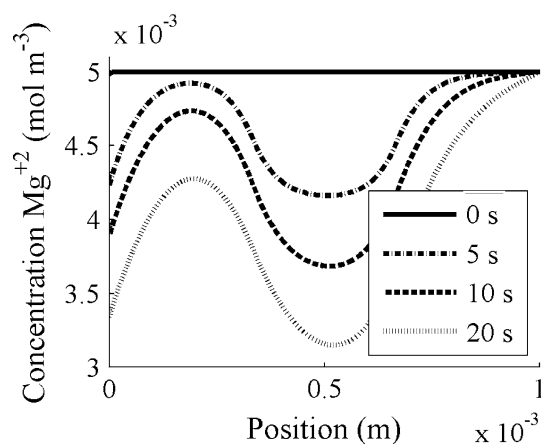


Fig. 13 Concentration of Mg^{2+} as a function of time and position for case C

4.2 Case B

Figures 6, 7, 8, 9 and 10 show the concentration of the different ions for different times. All methods gave the same results so only one of the solutions is shown.

As seen on Figs. 6, 7, 8 and 9, in case B the flux and current density are also fixed at the boundary $x = 0$ as was done for the case A, excepted than here, it is only for the chloride ion. There is no potential or concentration dependency at boundary for the fixed flux of chloride. It can be seen on Fig. 7 that the chloride ion concentration goes down very fast. As shown on Figs. 6 and 8, sodium cations are transported away from the boundary $x = 0$ at a faster rate than magnesium cations. This is the behaviour expected as sodium cation has a higher migration coefficient than the magnesium cation. As shown on Fig. 9, the transport of bromide ion towards the boundary $x = 0$ compensates the cationic charge to keep

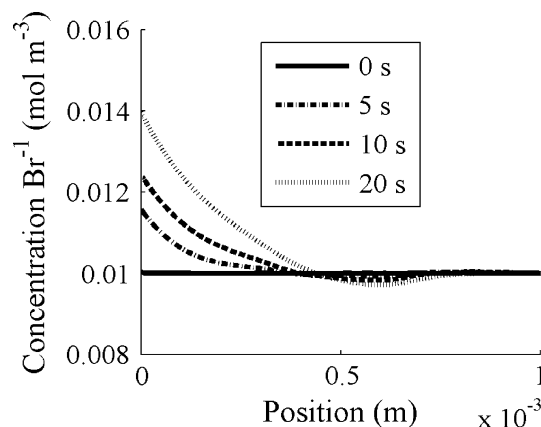


Fig. 14 Concentration of Br^{1-} as a function of time and position for case C

electroneutrality. The potential curves on Fig. 10 show that for most of the domain, the voltage drop is mostly linear.

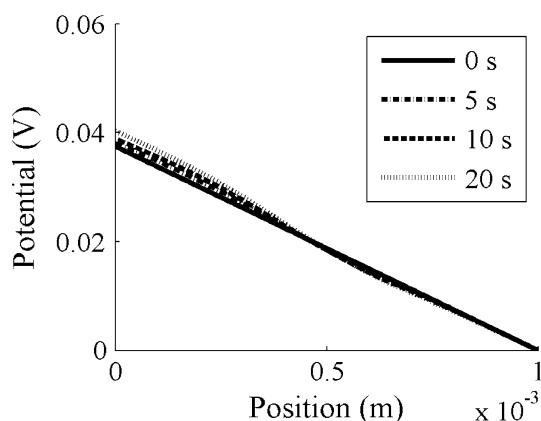


Fig. 15 Solution potential as a function of time and position for case C referred to a fixed potential of 0 V as a Dirichlet boundary condition at $x = L$

4.3 Case C

The Figs. 11, 12, 13 and 14 show the concentration of the different ions for different times. As all methods gave the same results, only one of the solutions is shown.

The case C is the same as case B for the boundary and initial conditions. The only difference from case B is the presence of a sink term for magnesium and bromide ions in the central third of the domain. The overall behaviour is the same as case B except near the central third of the domain.

Figure 11 shows that the chloride ion behaviour is dominated by the reaction boundary and the sink term. It can also be seen that the chloride ions decrease in the centre where the sink term is. As magnesium cations are removed in the same region (Fig. 13), their concentration is diminishing too. The magnesium ion is the slowest, and it is the transport of bromide ions that keeps electroneutrality (Fig. 14), while chloride ions are disappearing very fast. The Fig. 12 shows in the centre that the higher sodium ion concentration compensates the anions concentration thus helping to keep electroneutrality. Sodium ions also move outside the zone where chloride depletion is higher. Sodium ions also help to keep electroneutrality in the sink term zone but to a lesser extent than bromide ions.

The potential curves on Fig. 15 show that for most of the domain, the voltage drop is becoming nonlinear as opposed to case B. The nonlinear trend is asymmetric relative to the centre of the domain. The ions depleted zone towards the boundary at $x = 0$ is becoming more resistive relatively to the zone towards the opposite boundary. The conductivity variation follows the total ion concentration (see Fig. 11, 12, 13 and 14).

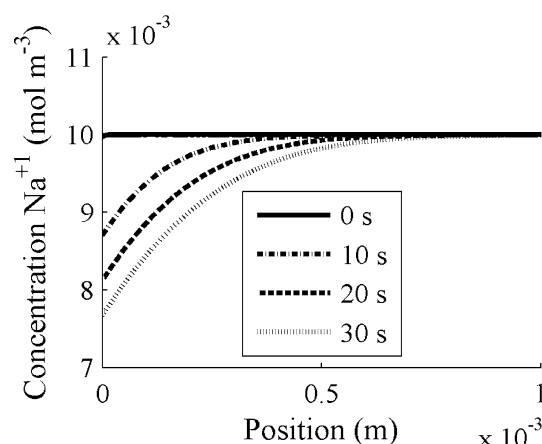


Fig. 16 Concentration of Na^{+} as a function of time and position for case D

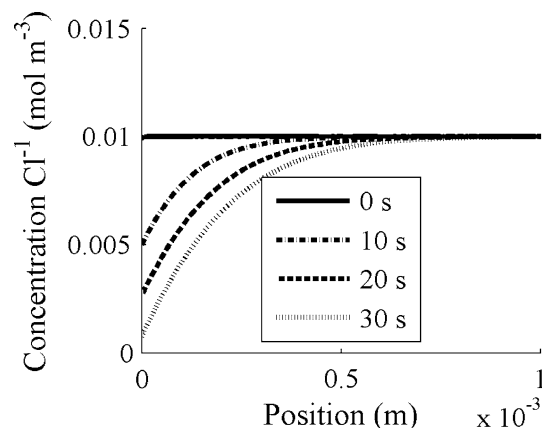


Fig. 17 Concentration of Cl^{-} as a function of time and position for case D

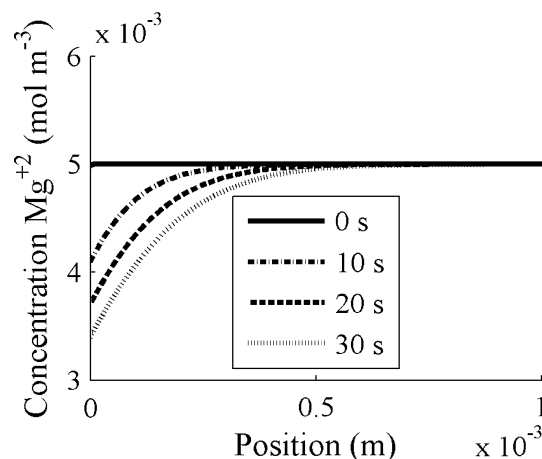


Fig. 18 Concentration of Mg^{2+} as a function of time and position for case D

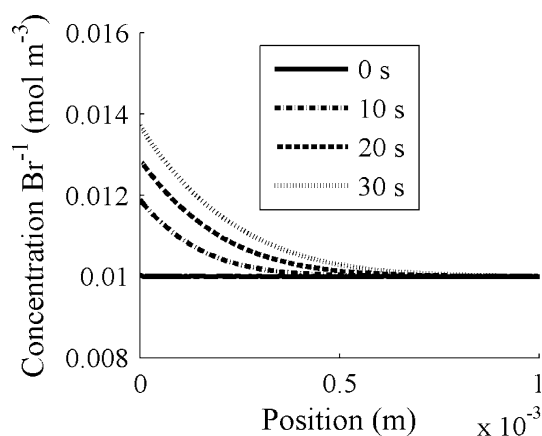


Fig. 19 Concentration of Br^{1-} as a function of time and position for case D

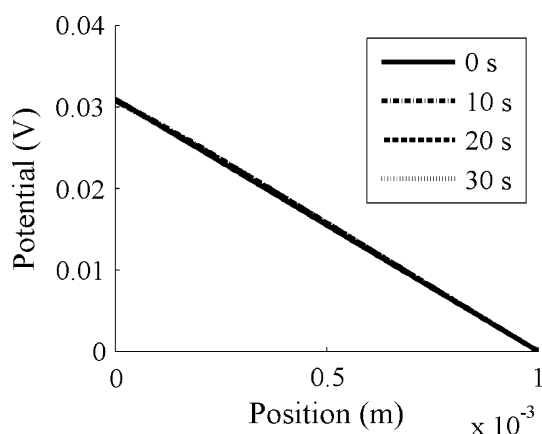


Fig. 20 Solution potential as a function of time and position for case D referred to a fixed potential of 0 V as a Dirichlet boundary condition at $x = L$

4.4 Case D

The Figs. 16, 17, 18 and 19 show the concentration of the different ions for different times. All methods gave the same results so only one of the solutions is shown. The only difference between case B and D is that the boundary condition for the chloride ion is defined by a nonlinear kinetic of Butler–Volmer kind. The ion concentration behaviour is similar to B, but the current density at boundary $x = 0$ is lower than in the case B which entrain an almost identical behaviour as case B but slower. It is to remember that, in the case B, the current density and chloride ion flux are fixed at the boundary $x = 0$ without any dependency on concentration or potential. The same comments apply to Fig. 20 showing the potential evolution as a function of time and position.

4.5 Case E

Figures 21, 22, 23, 24 and 25 show the concentration of the different ions at 100 s. The methods did not give the same

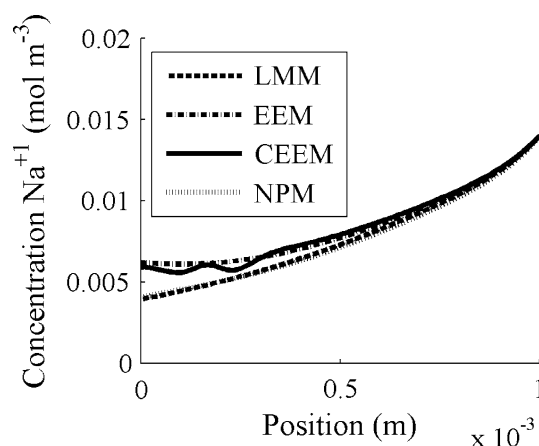


Fig. 21 Concentration of Na^{1+} as a function of position at time 100 s for case E

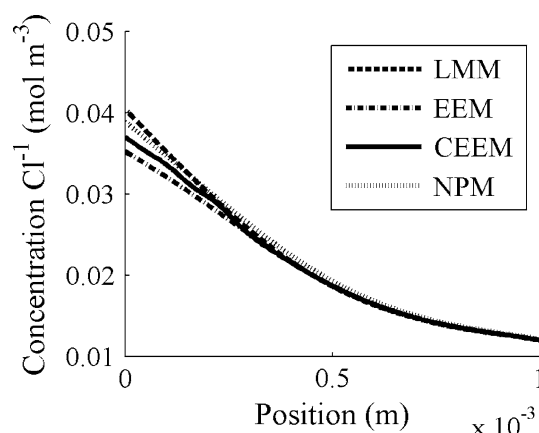


Fig. 22 Concentration of Cl^{1-} as a function of position at time 100 s for case E

results even if most curves have the same behaviour. The elimination procedure for electroneutrality implementation also generated some differences for a different choice of ion. Then, the curves shown in Figs. 21, 22, 23, 24, 25 and 26 are the average solution for each position in the domain. The number of solution used for calculating the average curve for the different methods is not the same for different causes. In the case of the Nernst–Planck application mode of COMSOL, only two solutions are available because it is not possible to eliminate ions from the ionic equilibrium as explained in the end of Sect. 3. For the EEM and CEEM methods, normally, five solutions are possible, but only four were available for CEEM method because of convergence problems with ion Fe^{2+} elimination choice. In the case of the LMM method, there is no elimination then only one solution is available. Later, in this section, the difference caused by the ions choice for elimination procedure will be discussed in more details. For all the methods, the equilibrium constant was respected with a maximum relative error of $\pm 3 \times 10^{-17} \%$.

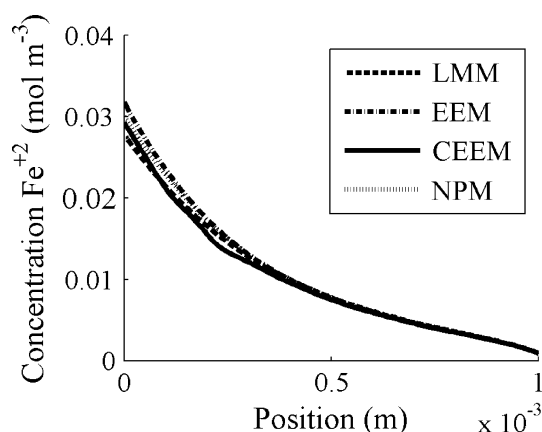


Fig. 23 Concentration of Fe^{2+} as a function of position at time 100 s for case E

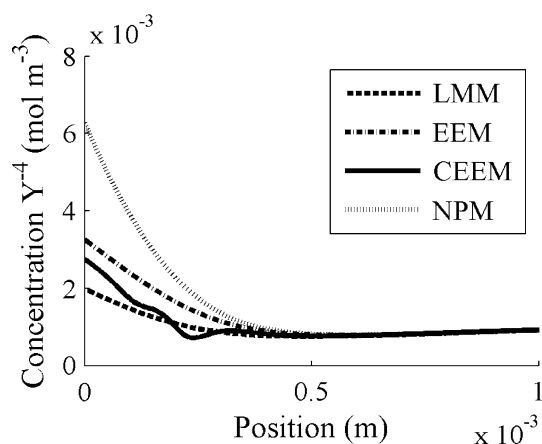


Fig. 24 Concentration of Y^{4-} as a function of position at time 100 s for case E

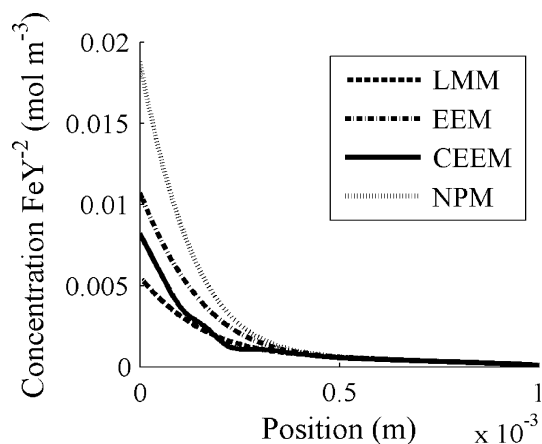


Fig. 25 Concentration of FeY^{2-} as a function of position at time 100 s for case E

As seen on Figs. 21, 22, 23, 24 and 25, in case E the flux and current density are fixed at the boundary $x = 0$ only for the ferrous ion. There is no potential or concentration

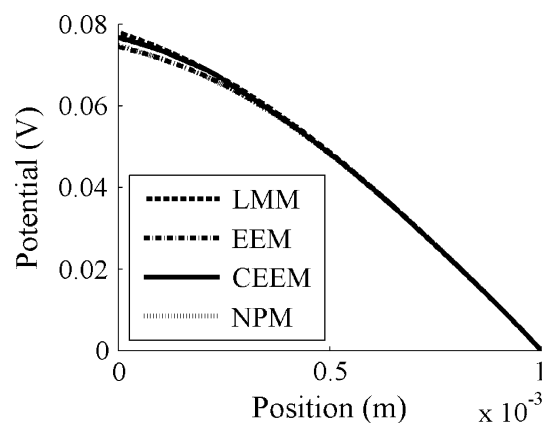


Fig. 26 Solution potential as a function of position at time 100 s for case E referred to a fixed potential of 0 V as a Dirichlet boundary condition at $x = L$

dependency at boundary for the fixed influx of ferrous ion. It can be seen on Figs. 21 and 22 that, for compensating the large ferrous positive charge influx (see Fig. 23), the chloride and sodium ions concentrations go up and down, respectively. These two ions are the faster and the most important to rapidly keep the system electroneutral. As shown on Fig. 23, the ion Fe^{2+} concentration near the boundary and over the domain is mostly rising with time. It is the most important flux from ions included in the equilibrium. The ferrous ion migration and diffusion flux are in the same direction. In the case of ion Y^{4-} , the diffusive flux is opposite to the migration flux. The relation between the flux of ions Y^{4-} and Fe^{2+} is mostly defining the evolution of FeY^{2-} concentration indirectly by the equilibrium relation. The ion FeY^{2-} concentration is mostly controlled by equilibrium because it has the lower transport properties and reacts relative to the other species. As shown on Fig. 25, the concentration is following the trend of the ferrous ion. Looking at Fig. 24, near the left boundary, the migration flux of Y^{4-} is keeping the ionic equilibrium at the expense of a diminution in concentration of Y^{4-} towards the other boundary. The strong flux of ferrous ion towards right boundary is keeping equilibrium, around the centre of the domain, where Y^{4-} is depleted. The potential curves on Fig. 26 show that for most of the domain, the voltage drop is following the ionic total concentration profile. The methods have a similar behaviour, but the difference between the lower curve and upper curve value at the boundary can be very significative. The lower difference is for the voltage curve and around 4.8 %. The difference for the ions Y^{4-} and FeY^{2-} are over 200 % which is a major difference. The latter fact can be possibly explained by the fact that the species are related to the ionic equilibrium implementation procedure. The difference for the ferrous ion is around 14 %, but its overall higher concentration can partially hide the perturbation effect. The

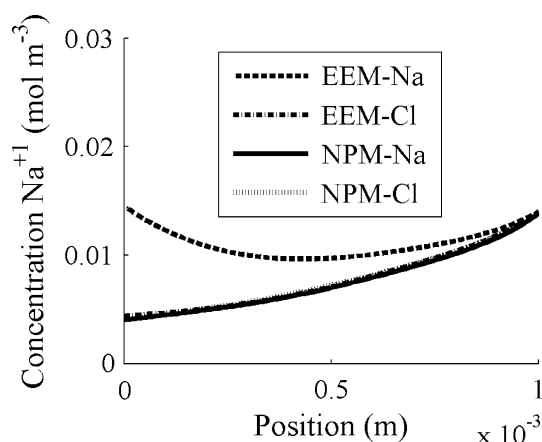


Fig. 27 Concentration of Na^{1+} as a function of position at time 100 s for case E using EEM and NPM methods with ion elimination of Na^{1+} or Cl^{1-}

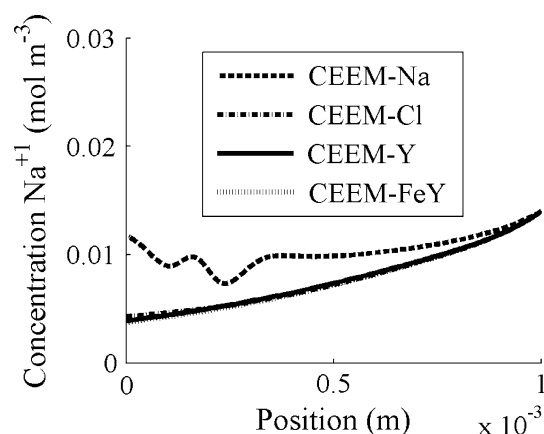


Fig. 28 Concentration of Na^{1+} as a function of position at time 100 s for case E using CEEM method with different choices of ion for the elimination procedure

most difficult variations to explain are for the sodium and chloride ions (around 58 and 14 %, respectively) which are not in the equilibrium reaction. This could be due to an indirect effect of the equilibrium implementation method but also an effect of the electroneutral implementation method. Effectively, the EEM method stays electroneutral, but the averaging curve hides a problem. The choice of species to be eliminated has an effect on the solution. The Fig. 27 shows the curve for case E when sodium or chloride is eliminated using EEM method. The curves are different and produce a different concentration gradient. Also shown are the curves for the COMSOL Nernst–Planck application mode. The result from COMSOL was more consistent but showed the worst performances for electroneutrality observation (see Table 7). The perturbation in the solution for the CEEM is only with the case where the sodium ion was chosen as the eliminated species as shown on Fig. 28. But it is to remember that it was not possible to obtain convergence for the case E when the ferrous ion is eliminated. For the CEEM method, it is possible to put the boundary condition explicitly for the ferrous ion by defining it as a function of the other species in the CEEM procedure. The equilibrium relation Eq. 42 is producing a nonlinear boundary condition function of other species. This is a much more difficult boundary condition to enforce, and this can explain the convergence problems.

All the methods have some difficulty to respect the boundary condition at the left boundary probably because the conditions are not in ionic equilibrium. Overall, the LMM method is more consistent for observing the boundary conditions on the left boundary. It could be argue that defining a finer mesh at the boundary zone can solve the problem, but it will not be practical as the domain for all the case is already small (1 mm), one dimension and the maximum quadratic element size is of 0.1 μm .

The Table 7 shows how well the different methods were able to respect electroneutrality over the domain. The given bounds mean that, for the electroneutrality equation, no point of the domain was outside the bound. For the cases A–D, all methods performed well and almost identically except for the LMM method which was less good by an average order of 10. In fact, the results for electroneutrality are in the range of the machine error for the computer used for the simulations. The precision truncature error is around 2.2×10^{-16} for the computer used in this study, and it was evaluated with the algorithm method [41].

For the case E, the LMM method and the COMSOL Nernst–Planck application mode did not performed well. The CEEM and EEM remain electroneutral comparatively to LMM and COMSOL Nernst–Planck application mode. There is not a big difference for voltage even if LMM and COMSOL are not electroneutral. It is difficult to conclude

Table 7 Electroneutrality $\sum_i z_i c_i(x, t)$ compliance for the different methods

Case	LMM	CEEM	EEM	NPM
A	$\pm 6.94 \times 10^{-17}$	$\pm 6.94 \times 10^{-18}$	$\pm 6.94 \times 10^{-18}$	$\pm 6.94 \times 10^{-18}$
B	$\pm 1.39 \times 10^{-17}$	$\pm 1.73 \times 10^{-18}$	$\pm 1.73 \times 10^{-18}$	$\pm 1.73 \times 10^{-18}$
C	$\pm 1.39 \times 10^{-17}$	$\pm 1.73 \times 10^{-18}$	$\pm 1.73 \times 10^{-18}$	$\pm 1.73 \times 10^{-18}$
D	$\pm 1.39 \times 10^{-17}$	$\pm 1.73 \times 10^{-18}$	$\pm 1.73 \times 10^{-18}$	$\pm 1.73 \times 10^{-18}$
E	$\pm 7 \times 10^{-5}$	$\pm 9.0 \times 10^{-18}$	$\pm 1.06 \times 10^{-17}$	$[-0.04, 0]$

Table 8 Time step efficiency for the different methods

Case	Real time for solving (s)				Number of time step			
	LMM	CEEM	EEM	NPM	LMM	CEEM	EEM	NPM
A	16.9	16.8	14.1	11.5	20	25	21	21
B	20.4	20.3	20.6	17.8	23	21	26	22
C	12.1	14.8	11.0	13.5	17	17	17	17
D	19.4	22.0	17.8	15.8	17	17	17	17
E	76	47	97	135	18	19	18	19

Table 9 Solver efficiency for the different methods

Case	Number of residual computed				Number of Jacobian computed				Number of linear systems computed			
	LMM	CEEM	EEM	NPM	LMM	CEEM	EEM	NPM	LMM	CEEM	EEM	NPM
A	36	49	40	43	11	14	12	12	36	49	40	43
B	45	40	64	44	13	12	15	13	45	40	64	44
C	26	26	26	26	9	9	9	9	26	26	26	26
D	38	40	40	40	10	10	10	10	39	41	41	41
E	36	37	34	38	11	12	11	15	36	37	34	38

for the case E, and more investigation are necessary for the effect of equilibrium method implementation combined to a chosen electroneutrality method.

The Tables 8 and 9 show the average efficiency of the different methods applied to all cases. The number of time step taken is equivalent for all methods. The CEEM and LMM are faster to solve the different problems. The LMM is slightly better for iteration number performances. Even if the performances are interesting, the problem of the best method is not clear because of the difference between the solutions. The performances of the different method can be function of the chosen electroneutrality and equilibrium implementation methods and the nature of the boundary conditions.

The different numerical experiments have shown that all the methods performed very well outside case E. As was discussed in the end of the mathematical and numerical models section, even if the boundary conditions are not explicitly applied, they should be respected for all the methods for the physico-chemical model used in this paper. This last fact was well observed in case A–D for EEM method as it should be. The last comment is irrelevant for the other two methods because they are using explicit boundary formulations.

The validity of the two new methods could be very useful because a preliminary results in [27] Gagnon and the case E showed that in a problem where an equilibrium reaction is enforced, it appears that the choice of species to be eliminated and the electroneutrality

methods chosen can have an effect on the final numerical solution. Further investigations will be done on the latter subject. Also, the explicit boundary formulation can facilitate the modelling of multiphysics problems involving a temperature field, multiple phases or other physical systems.

5 Conclusion

We presented two new methods for electroneutrality implementation that permit explicit boundary conditions on all species. The first method is based on the Lagrange multiplier and the second on variational principles. It was shown that they were analytically equivalent to the more standard method not using explicit boundary conditions. They were numerically successful with different kinds of problem such as Neuman, Dirichlet or nonlinear (Butler–Volmer kinetic) boundary conditions, a multiionic system and with a localized nonlinear rate equation. The variational method was more complex to implement than the Lagrange multiplier method. In the case of complex problems including chemical equilibrium between each ionic species, it was not conclusive and more investigations are necessary.

Acknowledgments The authors gratefully acknowledge the financial support provided by Alcoa Inc. and the Natural Sciences and Engineering Research Council of Canada.

Appendix

Details of the consistent elimination equation method (CEEM)

In this “Appendix,” the variational form W_c^1 defined in Eq. 19 applied to the CEEM is presented in detail. Eq. 19 is written in four parts as follows:

$$W_c^1 = \underbrace{\int \delta c_1 \frac{\partial c_1}{\partial t} dV}_{W_c^{1,1}} - \underbrace{\int \nabla \delta c_1 \cdot (-D_1 \nabla c_1) dV}_{W_c^{1,2}} - \underbrace{\int \nabla \delta c_1 \cdot (-z_1 c_1 u_1 F \nabla \Phi) dV}_{W_c^{1,3}} + \underbrace{\oint \delta c_1 \bar{J}_1 dA}_{W_c^{1,4}} \quad (44)$$

Using Eqs. 5–9, each term of Eq. 44 can be defined as follows:

$$W_c^{1,1} = \int \left(\frac{-1}{z_1} \sum_{i=2}^N z_i \delta c_i \right) \left(\frac{-1}{z_1} \sum_{j=2}^N z_j \frac{\partial c_j}{\partial t} \right) dV = \int \left(\sum_{i=2}^N z_i \delta c_i \right) \frac{1}{z_1^2} \left(\sum_{j=2}^N z_j \frac{\partial c_j}{\partial t} \right) dV \quad (45)$$

$$W_c^{1,2} = - \int \left(\frac{-1}{z_1} \sum_{i=2}^N z_i \nabla \delta c_i \right) \cdot \left[-D_1 \left(\frac{-1}{z_1} \sum_{j=2}^N z_j \nabla c_j \right) \right] dV = \int \left(\frac{D_1}{z_1^2} \sum_{i=2}^N z_i \nabla \delta c_i \right) \cdot \left[\sum_{j=2}^N z_j \nabla c_j \right] dV \quad (46)$$

$$W_c^{1,3} = - \int \left(\frac{-1}{z_1} \sum_{i=2}^N z_i \nabla \delta c_i \right) \cdot \left[-z_1 u_1 \left(\frac{-1}{z_1} \sum_{j=2}^N z_j c_j \right) F \nabla \Phi \right] dV = \int \left(\frac{u_1 F \nabla \Phi}{z_1} \sum_{i=2}^N z_i \nabla \delta c_i \right) \cdot \left[\sum_{j=2}^N z_j c_j \right] dV \quad (47)$$

$$W_c^{1,4} = \oint \delta c_1 \bar{J}_1 dA = - \oint \left(\frac{1}{z_1} \sum_{i=2}^N z_i \delta c_i \right) \bar{J}_1 dA \quad (48)$$

Equation 20 is written as follows:

$$W_c^i = \sum_{i=2}^N \left[\underbrace{\int \delta c_i \frac{\partial c_i}{\partial t} dV}_{W_c^{i,1}} - \underbrace{\int \nabla \delta c_i \cdot (-D_i \nabla c_i) dV}_{W_c^{i,2}} + \sum_{i=2}^N \left[\underbrace{- \int \nabla \delta c_i \cdot (-z_i c_i u_i F \nabla \Phi) dV}_{W_c^{i,3}} + \underbrace{\oint \delta c_i \bar{J}_i dA}_{W_c^{i,4}} \right] \right] \quad (49)$$

Combining similar terms from Eqs. 44 and 49 and using Eqs. 45–48, we can demonstrate that:

$$W_c^{i,1} + W_c^{1,1} = \sum_{i=2}^N \left[\int \delta c_i \frac{\partial c_i}{\partial t} dV + \int \left(\frac{1}{z_1^2} \sum_{i=2}^N z_i \frac{\partial c_i}{\partial t} \right) \left(\sum_{j=2}^N z_j \delta c_j \right) dV \right] = \sum_{i=2}^N \left[\int \delta c_i \left(\frac{\partial c_i}{\partial t} + \frac{z_i}{z_1^2} \left(\sum_{j=2}^N z_j \frac{\partial c_j}{\partial t} \right) \right) dV \right] = \int \langle \delta c_2 \quad \delta c_3 \quad \dots \quad \delta c_N \rangle [M] \begin{Bmatrix} \dot{c}_2 \\ \dot{c}_3 \\ \vdots \\ \dot{c}_N \end{Bmatrix} dV \quad (50)$$

$$W_c^{i,2} + W_c^{1,2} = \sum_{i=2}^N \left[\int \nabla \delta c_i \cdot (D_i \nabla c_i) dV + \int \left(\frac{1}{z_1} \sum_{i=2}^N z_i \nabla \delta c_i \right) \cdot \left(\frac{D_1}{z_1} \sum_{j=2}^N z_j \nabla c_j \right) dV \right] = \sum_{i=2}^N \left[\int \nabla \delta c_i \cdot \left(D_i \nabla c_i + \frac{z_i D_1}{z_1^2} \left(\sum_{j=2}^N z_j \nabla c_j \right) \right) dV \right] = \int \langle \nabla \delta c_2 \quad \nabla \delta c_3 \quad \dots \quad \nabla \delta c_N \rangle [D] \begin{Bmatrix} \nabla c_2 \\ \nabla c_3 \\ \vdots \\ \nabla c_N \end{Bmatrix} dV \quad (51)$$

$$W_c^{i,3} + W_c^{1,3} = \sum_{i=2}^N \left[\int \nabla \delta c_i \cdot (z_i c_i F u_i \nabla \Phi) dV + \int \left(\frac{u_1 F \nabla \Phi}{z_1} \sum_{i=2}^N z_i \nabla \delta c_i \right) \cdot \left[\left(\sum_{j=2}^N z_j c_j \right) \right] dV \right] = \sum_{i=2}^N \left[\int \nabla \delta c_i \cdot \left[z_i F \nabla \Phi \left(c_i u_i + \frac{u_1}{z_1} \sum_{j=2}^N z_j c_j \right) \right] dV \right] = \int \langle \nabla \delta c_2 \quad \nabla \delta c_3 \quad \dots \quad \nabla \delta c_N \rangle [G] \{ \nabla \Phi \} dV \quad (52)$$

$$W_c^{i,4} + W_c^{1,4} = \sum_{i=2}^N \left[\oint \delta c_i \bar{J}_i dA \right] - \oint \left(\frac{1}{z_1} \sum_{i=2}^N z_i \delta c_i \right) \bar{J}_1 dA = \sum_{i=2}^N \left[\oint \delta c_i \left(\bar{J}_i - \frac{z_i}{z_1} \bar{J}_1 \right) dA \right] = \oint \langle \delta c_2 \quad \delta c_3 \quad \dots \quad \delta c_N \rangle \begin{Bmatrix} \left(\bar{J}_2 - \frac{z_2}{z_1} \bar{J}_1 \right) \\ \left(\bar{J}_3 - \frac{z_3}{z_1} \bar{J}_1 \right) \\ \vdots \\ \left(\bar{J}_N - \frac{z_N}{z_1} \bar{J}_1 \right) \end{Bmatrix} dA \quad (53)$$

$$W_\Phi = \int \langle \nabla \delta \Phi \rangle [Z] \left\{ \begin{array}{c} \nabla c_2 \\ \nabla c_3 \\ \vdots \\ \nabla c_N \end{array} \right\} + \langle \nabla \delta \Phi \rangle Q \{ \nabla \Phi \} dV + \oint \delta \Phi \bar{i} dA \quad (54)$$

The matrices introduced previously are defined as follows:

$$[M]_{(N-1) \times (N-1)} = [I] + \left\{ \begin{array}{c} \frac{z_2}{z_1} \\ \frac{z_3}{z_1} \\ \vdots \\ \frac{z_N}{z_1} \end{array} \right\} \left\langle \begin{array}{ccc} \frac{z_2}{z_1} & \frac{z_3}{z_1} & \cdots & \frac{z_N}{z_1} \end{array} \right\rangle \quad (55)$$

$$\{\delta c\} = [P] \{\delta c_n\}_{n(N-1) \times 1} \quad (61)$$

$$\begin{aligned} \langle c_n \rangle &= \langle \langle c_n \rangle_2 \quad \langle c_n \rangle_3 \quad \cdots \quad \langle c_n \rangle_{N-1} \quad \langle c_n \rangle_N \rangle \\ \langle \delta c_n \rangle &= \langle \langle \delta c_n \rangle_2 \quad \langle \delta c_n \rangle_3 \quad \cdots \quad \langle \delta c_n \rangle_{N-1} \quad \langle \delta c_n \rangle_N \rangle \\ \langle \nabla c \rangle &= \langle \langle \nabla c_2 \rangle \quad \langle \nabla c_3 \rangle \quad \cdots \quad \langle \nabla c_{N-1} \rangle \quad \langle \nabla c_N \rangle \rangle \end{aligned} \quad (62)$$

$$\begin{aligned} [B] &= \begin{bmatrix} [b] & [0] & [0] & \cdots \\ [0] & [b] & [0] & \cdots \\ [0] & [0] & \ddots & \cdots \\ \cdots & \cdots & \cdots & [b] \end{bmatrix}_{3(S-1) \times n(S-1)}; \\ [b] &= \begin{bmatrix} S_{1,x} & S_{2,x} & \cdots & S_{n,x} \\ S_{1,y} & S_{2,y} & \cdots & S_{n,y} \\ S_{1,z} & S_{2,z} & \cdots & S_{n,z} \end{bmatrix}_{3 \times n} \end{aligned} \quad (63)$$

$$[D]_{3(N-1) \times 3(N-1)} = \begin{bmatrix} \left(D_2 + \frac{z_2^2}{z_1^2} D_1\right) [I_{3 \times 3}] & \frac{z_2 z_3}{z_1^2} D_1 [I_{3 \times 3}] & \cdots & \frac{z_2 z_N}{z_1^2} D_1 [I_{3 \times 3}] \\ & \left(D_3 + \frac{z_3^2}{z_1^2} D_1\right) [I_{3 \times 3}] & & \frac{z_3 z_N}{z_1^2} D_1 [I_{3 \times 3}] \\ & \text{sym} & \ddots & \vdots \\ & & & \left(D_N + \frac{z_N^2}{z_1^2} D_1\right) [I_{3 \times 3}] \end{bmatrix} \quad (56)$$

$$[G]_{3(N-1) \times 3} = F \begin{bmatrix} \left(\left(u_2 z_2 + \frac{u_1}{z_1} z_2^2 \right) c_2 + \frac{u_1}{z_1} z_2 z_3 c_3 + \cdots + \frac{u_1}{z_1} z_2 z_N c_N \right) [I]_{3 \times 3} \\ \left(\frac{u_1}{z_1} z_3 z_2 c_2 + \left(u_3 z_3 + \frac{u_1}{z_1} z_3^2 \right) c_3 + \cdots + \frac{u_1}{z_1} z_3 z_N c_N \right) [I]_{3 \times 3} \\ \vdots \\ \left(\frac{u_1}{z_1} z_N z_2 c_2 + \frac{u_1}{z_1} z_N z_3 c_3 + \cdots + \left(u_N z_N + \frac{u_1}{z_1} z_N^2 \right) c_N \right) [I]_{3 \times 3} \end{bmatrix} \quad (57)$$

$$\begin{aligned} [Z]_{3 \times 3(N-1)} &= \begin{bmatrix} K_2 [I]_{3 \times 3} & K_3 [I]_{3 \times 3} & & \\ \cdots & K_{N-1} [I]_{3 \times 3} & K_N [I]_{3 \times 3} & \end{bmatrix} \\ K_i &= F z_i (D_i - D_1) \\ Q &= F^2 \sum_{i=2}^N [(z_i u_i - z_1 u_1) z_i c_i] \end{aligned} \quad (58)$$

Using classical finite element formulation, it can be shown that the following relations hold [30, 31] at the element level with “ n ” nodes:

$$\begin{aligned} c_i &= \langle S \rangle \{c_n\}_i; \quad \delta c_i = \langle S \rangle \{\delta c_n\}_i; \\ \{\nabla c\} &= [B] \{c_n\}_{n(N-1) \times 1}; \\ \{\nabla \delta c\} &= [B] \{\delta c_n\}_{n(N-1) \times 1} \end{aligned} \quad (59)$$

$$\begin{aligned} \Phi &= \langle S \rangle \{\Phi_n\}; \quad \delta \Phi = \langle S \rangle \{\delta \Phi_n\}; \\ \{\nabla \Phi\} &= [b] \{\Phi_n\}_{n \times 1}; \quad \{\nabla \delta \Phi\} = [b] \{\delta \Phi_n\}_{n \times 1} \end{aligned} \quad (60)$$

$$[P] = \begin{bmatrix} \langle S \rangle & [0] & [0] & \cdots \\ [0] & \langle S \rangle & [0] & \cdots \\ [0] & [0] & \ddots & \cdots \\ \cdots & \cdots & \cdots & \langle S \rangle \end{bmatrix}_{(S-1) \times n(S-1)} \quad (64)$$

where $\langle S \rangle$ are the classical shape functions and $\{c_n\}_i$, the nodal values on the species i and n is the number of nodes. Using those relations, we can write the following discrete relation corresponding to Eq. 27:

$$W = \sum_{e=1}^{\text{Nelt}} (W_c^e + W_\Phi^e) = 0 \quad (65)$$

$$\begin{aligned} W_c^e &= \langle \delta c_n \rangle \int_{V^e} ([M] \{\dot{c}_n\} + [B]^T [D] [B] \{c_n\} \\ &\quad + [B]^T [G] [b] \{\Phi_n\}) dV + \langle \delta c_n \rangle \oint_{\Gamma_N^e} [P]^T \{\bar{J}_n\} dA \end{aligned} \quad (66)$$

$$W_{\Phi}^e = \langle \delta \Phi_n \rangle \int_{V^e} ([b]^T [Z] [B] \{c_n\} + Q[b]^T [b] \{\Phi_n\}) dV + \langle \delta \Phi_n \rangle \oint_{\Gamma_N^e} \{S\} \bar{i} dA \quad (67)$$

Equivalence between CEEM and LMM

In this “Appendix,” it is shown that CEEM and LMM are analytically equivalent. First we choose to define λ as a function of species one:

$$\lambda = \frac{-1}{z_1} \left[\frac{\partial c_1}{\partial t} + \nabla \cdot (-D_1 \nabla c_1 - u_1 z_1 F c_1 \nabla \Phi) \right] = \frac{-1}{z_1} \left[\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right] \quad (68)$$

Second, the Eq. 34 is presented anew with the species conservation equation for species one in evidence and with insertion of definition (68):

$$W = \sum_{i=2}^N \left[\int \delta c_i \left(\frac{\partial c_i}{\partial t} + \frac{-z_i}{z_1} \left[\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right] \right) - \nabla \delta c_i \cdot (-D_i \nabla c_i - z_i c_i u_i F \nabla \Phi) dV \right] + \sum_{i=2}^N \oint \delta c_i \vec{J}_i dA \int \delta c_1 \left(\frac{\partial c_1}{\partial t} + \frac{-1}{z_1} \left[\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right] \right) - \nabla \delta c_1 \cdot \vec{J}_1 dV + \oint \delta c_1 \vec{J}_1 dA + \int \delta \lambda \left(\sum_{i=1}^N z_i c_i \right) dV + W_{\Phi} = 0 \quad (69)$$

Using divergence theorem and integration by parts, the simplified form of Eq. 69 is obtained:

$$W = \sum_{i=2}^N \left[\int \delta c_i \left(\frac{\partial c_i}{\partial t} - \frac{z_i}{z_1} \left[\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right] \right) + \delta c_i \nabla \cdot \vec{J}_i dV \right] + \int \delta \lambda \left(\sum_{i=1}^N z_i c_i \right) dV + W_{\Phi} = 0 \quad (70)$$

It can be seen that the equation system 70 is the same as associated with Eq. 30 of CEEM method except for the presence of the electroneutrality term. The electroneutrality term can be transformed back to the eliminated equation associated with species one. This will show that equation system (70) can be transformed back to the original problem which will prove that CEEM and LMM are equivalent. First, we take the first variation of Eq. 68:

$$\delta \lambda = \frac{-1}{z_1} \left[\delta \left(\frac{\partial c_1}{\partial t} \right) + \delta (\nabla \cdot \vec{J}_1) \right] \quad (71)$$

Second, we substitute (71) in the electroneutrality term of (70):

$$\int \delta \lambda \left(\sum_{i=1}^N z_i c_i \right) dV = \int \left(\frac{-1}{z_1} \left[\delta \left(\frac{\partial c_1}{\partial t} \right) + \delta (\nabla \cdot \vec{J}_1) \right] \right) \left(\sum_{i=1}^N z_i c_i \right) dV \quad (72)$$

If we expand (72) to bring all the terms in function of c_1 , we obtain the following equation:

$$\begin{aligned} & \int \left(\frac{-1}{z_1} \left[\delta \left(\frac{\partial c_1}{\partial t} \right) + \delta (\nabla \cdot \vec{J}_1) \right] \right) \left(\sum_{i=1}^N z_i c_i \right) dV \\ &= \int \left(\frac{-1}{z_1} \left[\delta \left(\frac{\partial c_1}{\partial t} \right) + \delta (\nabla \cdot \vec{J}_1) \right] \right) \left(c_1 z_1 + \sum_{i=2}^N z_i c_i \right) dV \\ &= \int \left(\frac{-1}{z_1} \left[\delta \left(\frac{\partial c_1}{\partial t} \right) + \delta (\nabla \cdot \vec{J}_1) \right] \right) c_1 z_1 \\ &\quad - \frac{1}{z_1} \left[\delta \left(\frac{\partial c_1}{\partial t} \right) + \delta (\nabla \cdot \vec{J}_1) \right] \left(\sum_{i=2}^N z_i c_i \right) dV \\ &= \int \left(-c_1 \delta \left(\frac{\partial c_1}{\partial t} \right) - c_1 \delta (\nabla \cdot \vec{J}_1) \right. \\ &\quad \left. - \frac{1}{z_1} \left[\delta \left(\frac{\partial c_1}{\partial t} \right) + \delta (\nabla \cdot \vec{J}_1) \right] (-c_1 z_1) \right) dV \\ &= \int \left(-c_1 \delta \left(\frac{\partial c_1}{\partial t} \right) - c_1 \delta (\nabla \cdot \vec{J}_1) + c_1 \delta \left(\frac{\partial c_1}{\partial t} \right) \right. \\ &\quad \left. + c_1 \delta (\nabla \cdot \vec{J}_1) \right) dV \quad (73) \end{aligned}$$

The final line of Eq. 73 leads to zero, which proves that the CEEM and LMM are equivalent. It is possible to pursue the demonstration to obtain the species one conservation equation, thus showing that the system is equivalent to the original set of equation without electroneutrality implemented. By using the following relation:

$$\delta \left[c_1 \frac{\partial c_1}{\partial t} + c_1 \nabla \cdot \vec{J}_1 \right] = \delta c_1 \left[\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right] + c_1 \delta \left[\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right] \quad (74)$$

we can transform the last line of (73):

$$\begin{aligned} & \int \left(-c_1 \delta \left(\frac{\partial c_1}{\partial t} \right) - c_1 \delta (\nabla \cdot \vec{J}_1) + c_1 \delta \left(\frac{\partial c_1}{\partial t} \right) + c_1 \delta (\nabla \cdot \vec{J}_1) \right) dV \\ &= \int \left(-\delta \left(c_1 \frac{\partial c_1}{\partial t} + c_1 \nabla \cdot \vec{J}_1 \right) + \delta c_1 \left(\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right) \right. \\ &\quad \left. + c_1 \delta \left(\frac{\partial c_1}{\partial t} \right) + c_1 \delta (\nabla \cdot \vec{J}_1) \right) dV = \int \left(\delta c_1 \left(\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right) \right. \\ &\quad \left. - \delta \left(c_1 \left(\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right) \right) + c_1 \delta \left(\frac{\partial c_1}{\partial t} + \nabla \cdot \vec{J}_1 \right) \right) dV \quad (75) \end{aligned}$$

Observing Eq. 75, we can remove the two last variational contributions by continuity and obtain the original species conservation equation for species one with the associated test function.

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